Supporting Information

Critical Role of Explicit Inclusion of Solvent and Electrode Potential in Electrochemical Description of Nitrogen Reduction

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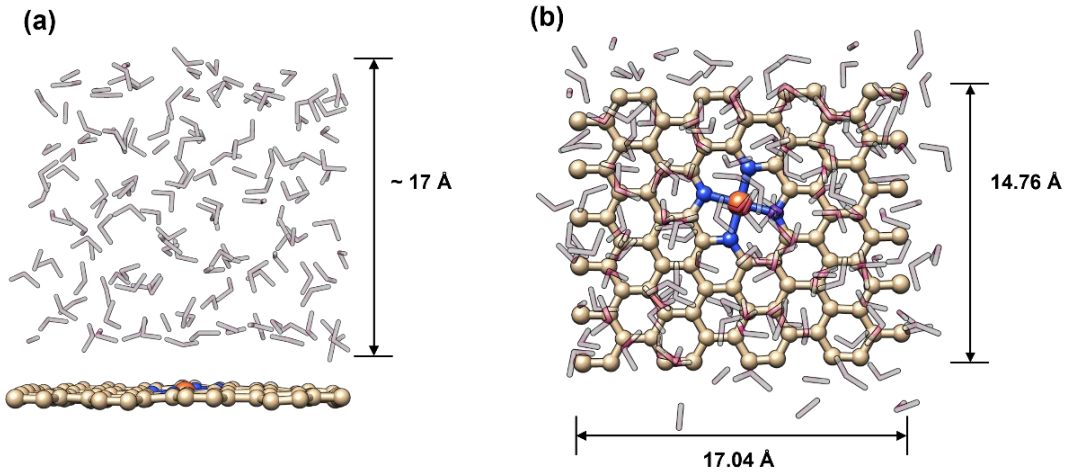


Figure S1. The side view (a) and top view (b) of Fe-N_4-C catalyst model in liquid phase system at PZC. The C, N, Fe, O, H atoms are denoted as ginger, blue, orange, pink and white spheres, respectively.

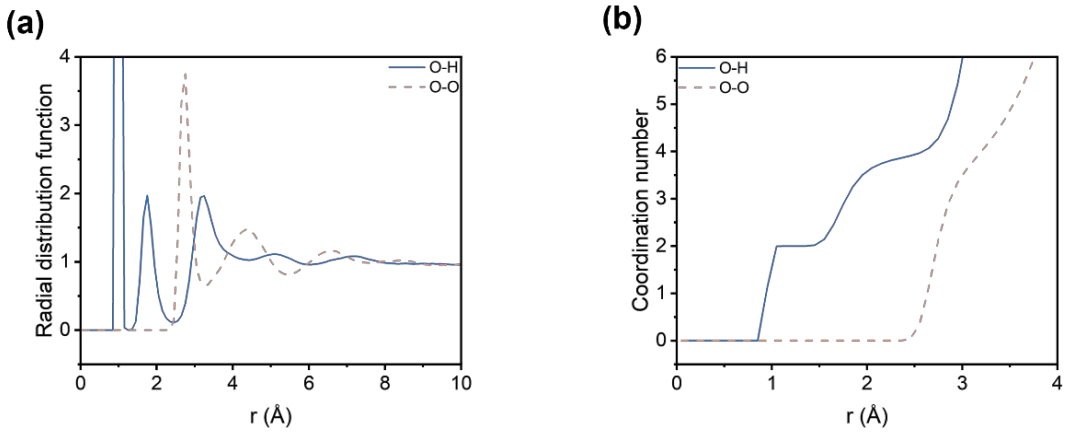


Figure S2. Radial distribution function of water from equilibrated AIMD trajectory. (a) The radial distribution function (RDF) of O-H and O-O and (b) the coordination number (integrated RDF) of O-H and O-O.

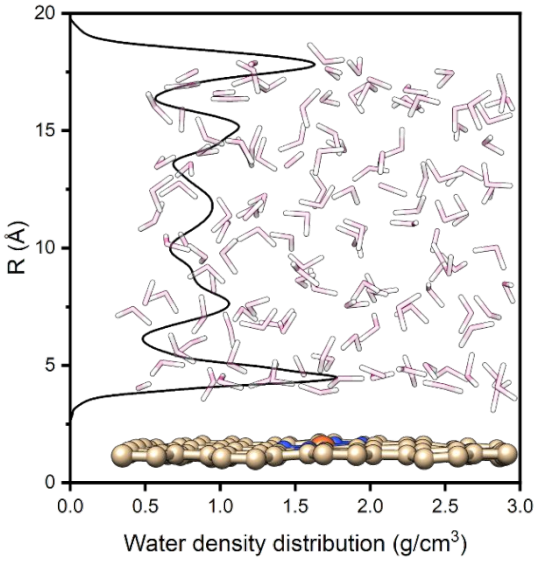


Figure S3. The water density distribution along the surface perpendicular from equilibrated AIMD trajectories.

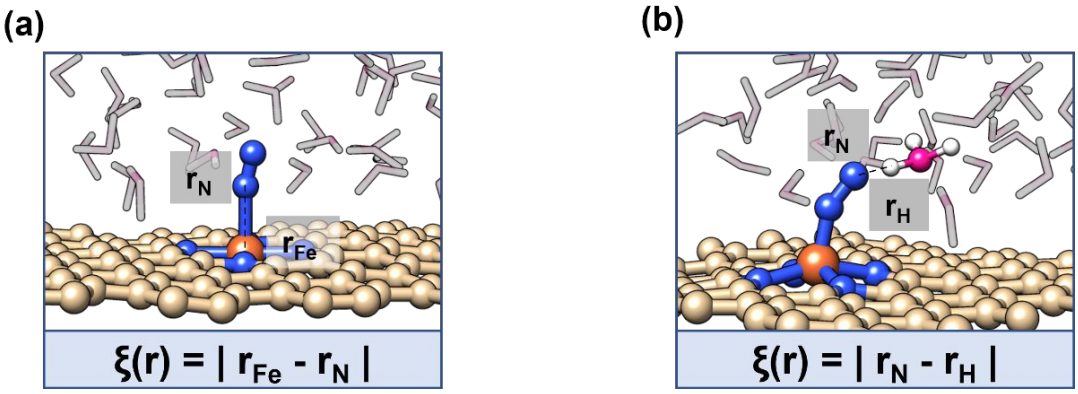


Figure S4. The illustrations of reaction coordinates for the (a) N_2 adsorption, (b) *N_2 first protonation. The C, N, Fe, O, H atoms are denoted as ginger, blue, orange, pink and white spheres, respectively.

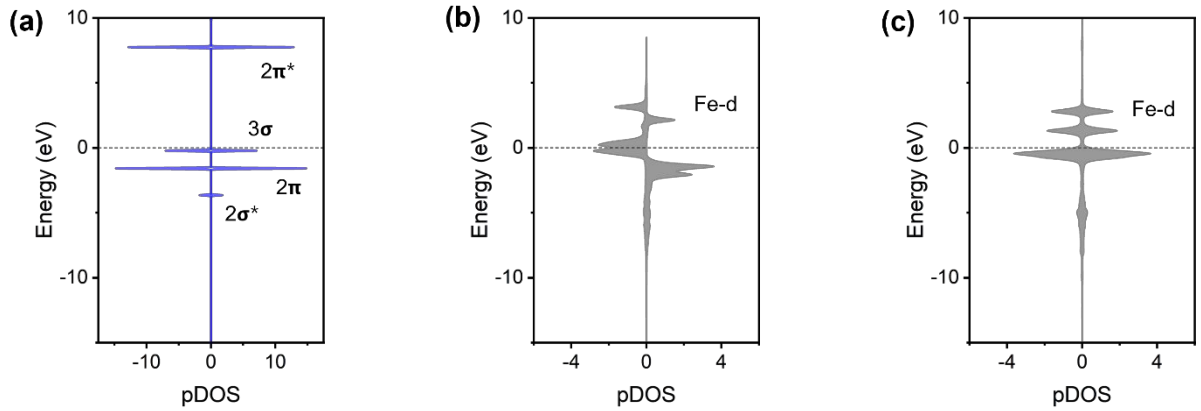


Figure S5. (a) pDOS for free N_2, Fe-N_4-C before N_2 adsorption in clean system (b) and liquid system (c).

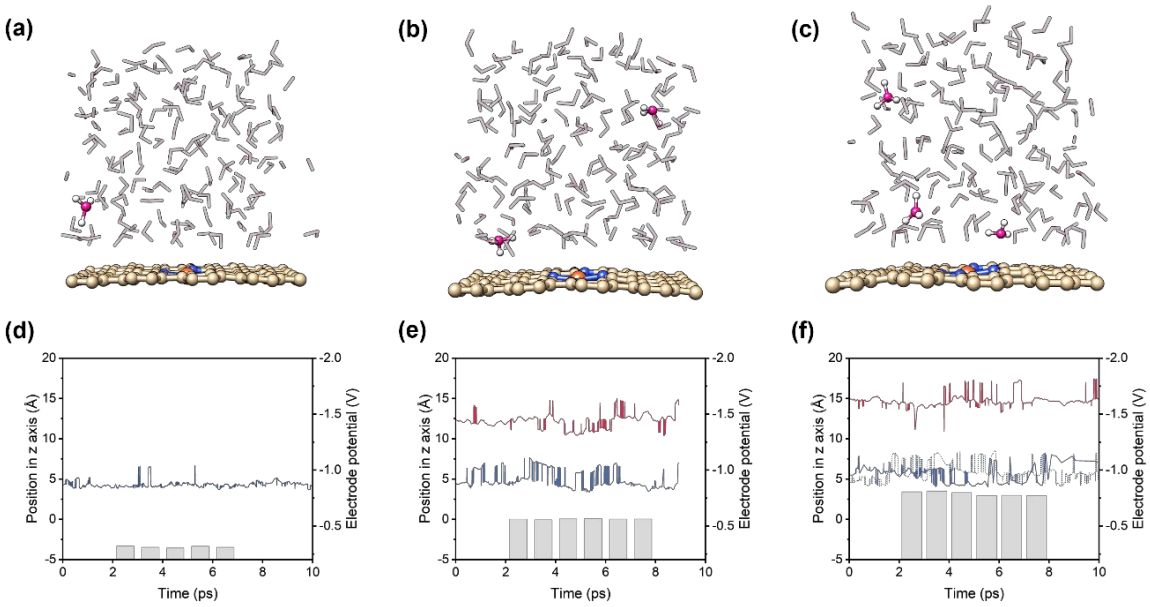


Figure S6. The snapshots of the Fe-N_4-C/water interfaces of the system containing (a) 1, (b) 2 and (c) 3 H_3O^+. The position variation in z direction of H_3O^+ and the corresponding electrode potential variation in systems containing different amounts of H_3O^+. (d), (e), and (f) respectively correspond to the system containing 1, 2 and 3 H_3O^+. (Bar for electrode potential and line for position in z axis)

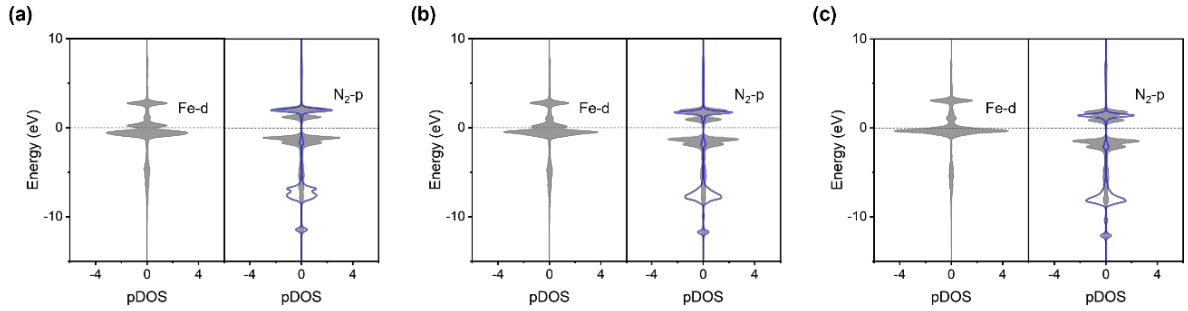


Figure S7. pDOS of liquid system with different potential before and after N_2 adsorption. ((a) for -0.23 V; (b) for -0.48 V and (c) for -0.68 V)

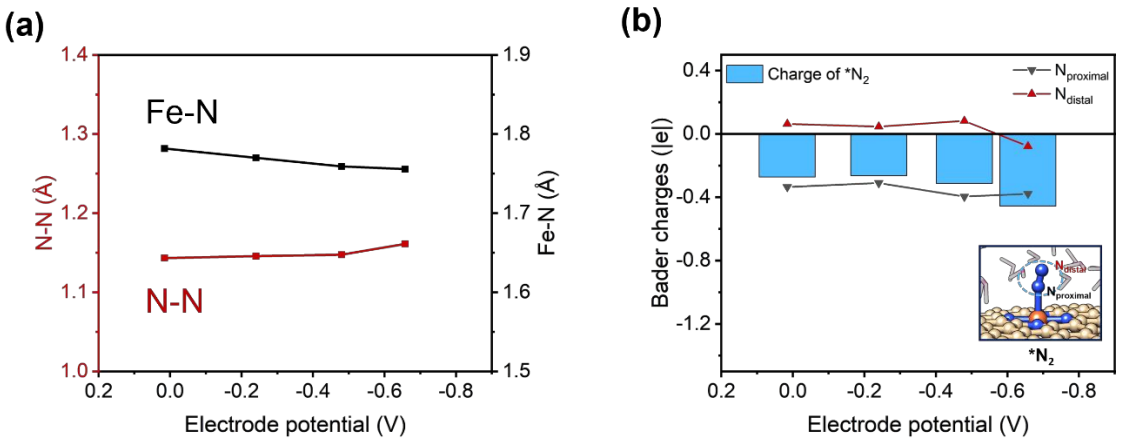


Figure S8. Bond length variation of N-N and Fe-N (a); Bader charge variation of the adsorbate *N_2 (b) under different electrode potential by adding K counterions.

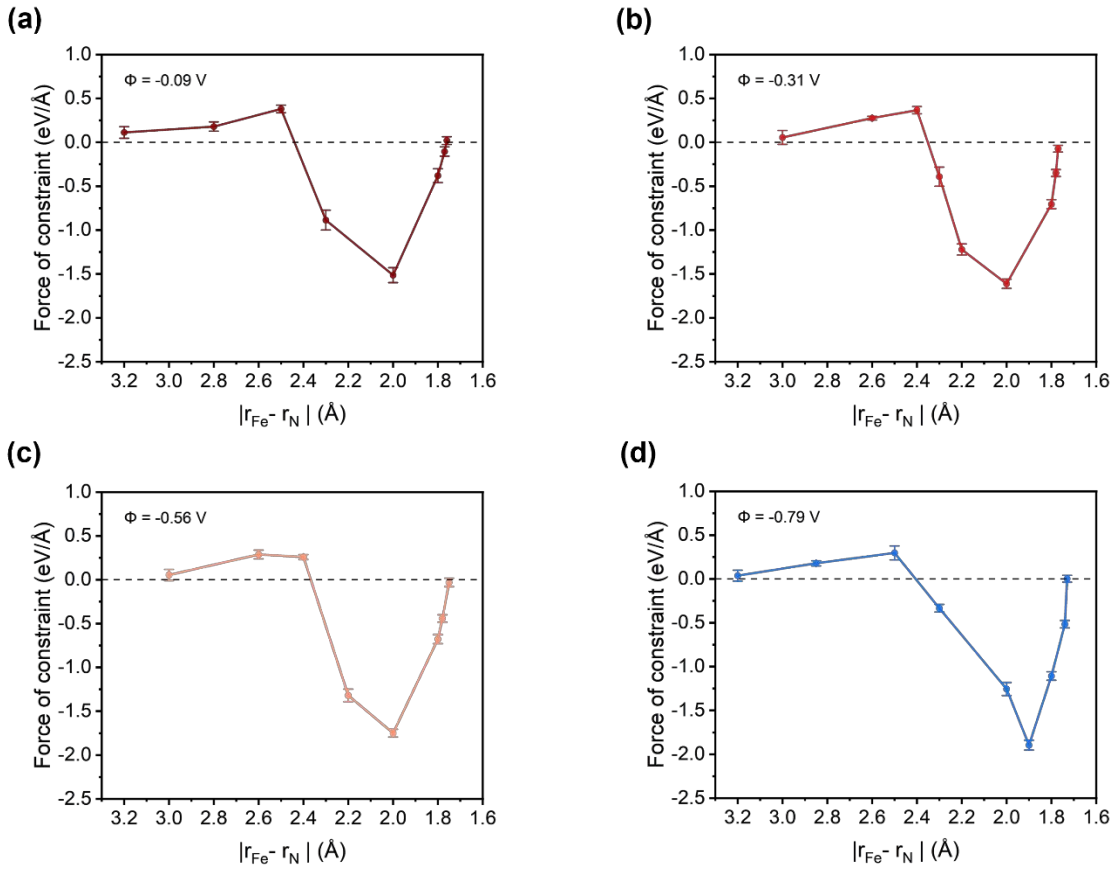


Figure S9. The averaged force of constrained MD simulations for the N_2 adsorption at (a) -0.09 V, (b) -0.31 V, (c) -0.56 V and (d) -0.79 V vs RHE. The error bars were in correspond to margins of error calculated considering a 95% confidence level.

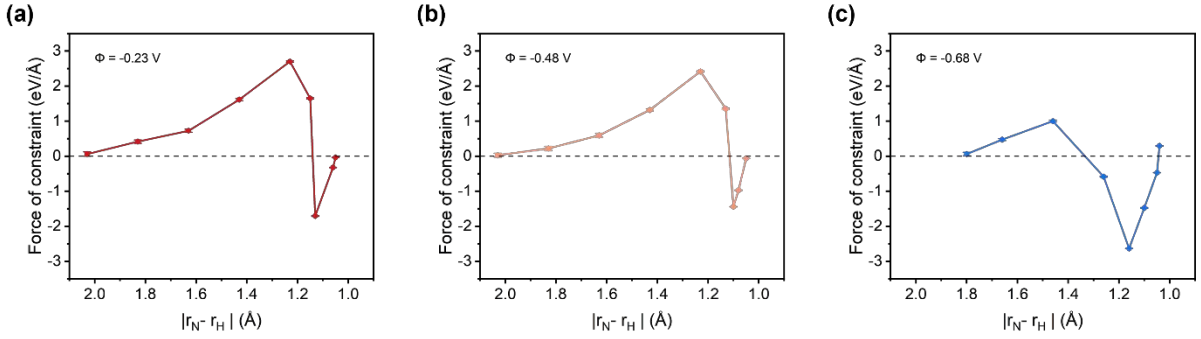


Figure S10. The averaged force of constrained MD simulations for the N_2 first protonation at (a) -0.23 V, (b) -0.48 V and (c) -0.68 V vs. RHE. The error bars were in correspond to margins of error calculated considering a 95% confidence level.

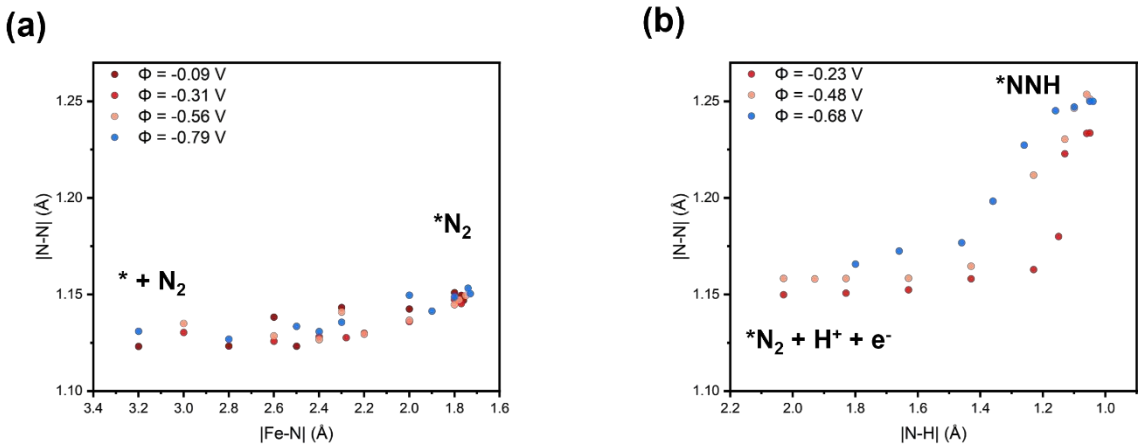


Figure S11. The N-N distances along the reaction paths of the N_2 adsorption (a) and first protonation (b) reactions under different electrode potentials.

Table S1. Summary of the reported Fe-N_x-C catalysts for NRR at low temperature. The maximum yield rate, maximum faradaic efficiency (FE) and the electrode potential (U) at the maximum yield rate are shown

Catalyst	Electrolyte	NH_3 yield	FE (%)	U vs. RHE (V)
FeSA-N-C	0.1 M KOH	7.48 μg h^{-1}mgcat^{-1}	56.55	0.0
ISAS-Fe/NC	0.1 M PBS	62.9 μg h^{-1} mgcat^{-1}	18.6	-0.4
FePc/C	0.1 M Na_2SO_4 (pH = 6.8)	137.95μg h^{-1}mgcat^{-1}	10.5	-0.3
Fe-N/C-CNT	0.1 M KOH	34.83 μg h^{-1}mgcat^{-1}	9.28	-0.2
Fe_1-N-C	0.1 M KOH	1.56×10^{-11} mol $cm^{-2}s^{-1}$	4.51	-0.05

Table S2. Adsorption structures and the corresponding optimized energies of *N_2 on the Fe-N_4-C catalyst. (Orange atom is Fe, blue atom is N, ginger atom is C and white atom is H.)

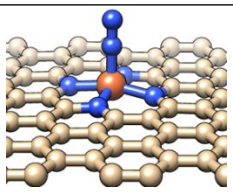
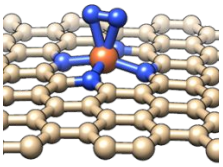
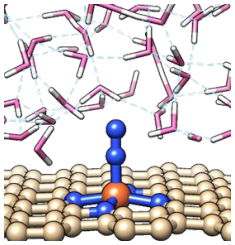
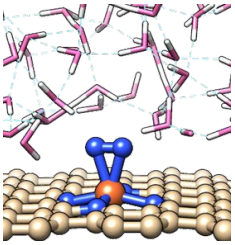
	end-on		**side-on**	
system	configuration	Energy/eV	configuration	Energy/eV
clean		-896.63		-895.73
liquid		-2997.46		-2996.51

Table S3. Adsorption Gibbs free energy of H_2 under different electrode potential.

Electrode potential	Adsorption Energy/eV
0.02	0.28
-0.22	-0.02
-0.50	-0.35
-0.76	-0.59

Table S4. Electrode potential of the initial state (U_{IS}), final state (U_{FS}) for various electrochemical reactions at different potentials. The variation of surface charge (Δq) during reactions and the free energy corrections for constant potential ($(\Delta U \cdot \Delta q)/2$, $\Delta U = U_{IS} - U_{FS}$) proposed by Nørskov et al. are also presented at list.

Reaction	U_{IS} (V)	U_{FS} (V)	$\triangle q$ (|e|)	$\|(\triangle U \cdot \triangle q) / 2\|$ (eV)
N_2 adsorption (No counterions)	-0.09	0.02	0.35	0.02
N_2 adsorption ($1H^+$)	-0.31	-0.23	0.28	0.01
N_2 adsorption ($2H^+$)	-0.56	-0.48	0.27	0.01
N_2 adsorption ($3H^+$)	-0.79	-0.68	0.31	0.01
N_2 first protonation ($1H^+$)	-0.23	0.06	0.96	0.14
N_2 first protonation ($2H^+$)	-0.48	-0.13	1.16	0.20
N_2 first protonation ($3H^+$)	-0.69	-0.38	1.02	0.16